PYROLYSIS OF SURFACE-IMMOBILIZED MODEL COMPOUNDS.
MECHANISTIC IMPLICATIONS FOR THE THERMAL CHEMISTRY OF COAL

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INTRODUCTION

The thermal reactivity of coal forms the basis of many processes devised for coal utilization. Although much is known about the kinetics of coal pyrolysis,[1] a detailed molecular level mechanistic understanding is hampered by the complex chemical structure of coal. Organic compounds[2] and simple polymers[3] have been employed beneficially as surrogates for coal in many studies of thermal and chemical reactivity. However, the interpretive extrapolation of such model compound behavior to coal should take into consideration some of the complexities inherent to coal.

Our research has been investigating the potential role that the cross-linked network structure of coal may play in perturbing free-radical reactions associated with coal thermolysis.[4-7] This may be particularly important in the thermal conversion of coal at low temperatures, e.g., 350-400°C, where bonds begin to break but most of the residual framework is retained. In order to assess the potential impact of restricted transport on thermal reaction pathways, we have modeled the phenomenon experimentally by studying organic model compounds that are covalently linked to an inert silica surface. The experimental methodology and significant results from studies of the thermolysis of surface-attached Ph(CH₂)ₙPh [n = 0-4] at 345-400°C will be briefly surveyed. Initial results from studies of two-component surfaces will also be presented that reveal the role of radical migration, via facile hydrogen shuttling, in modifying the effects of diffusional constraints.

RESULTS AND DISCUSSION

Surface Attachment Methodology. The criteria for an appropriate support and covalent link are substantial. Both must be stable in the temperature range of interest (ca. 400°C). The support should have a moderately high surface area with enough active sites for attaching significant quantities of the organic moieties of interest. Any unreacted surface sites should not be catalytically active. Furthermore, the position of surface attachment within the organic moiety should be somewhat remote from the normal position of thermal reactivity. Finally, although the covalent link should be thermally stable, there must be a facile method for quantitative analysis of surface-bound reactants and products.

These criteria were met through the use of a high-purity, nonporous, amorphous fumed silica as the support and a Si-O-C$_{aryl}$ linkage as the surface connection. The surface attachment reaction is shown in Fig. 1, and the full experimental details are given elsewhere.[4,5] In short, the standard procedure for preparation of saturation coverage samples was to disperse an excess of the parent phenol onto predried silica by evaporating benzene solvent from a slurry, to heat the resulting powder at 225°C in a sealed, degassed tube to effect the surface reaction, and to evacuate the product at 270°C to remove excess phenol and the water byproduct. Lower surface

coverages were prepared by limiting the amount of phenol relative to the surface hydroxyl population. As shown in Fig. 1, surface coverages were analyzed by a procedure that involves recovery of the phenol following digestion of the silica in aqueous base. Saturation surface coverages of 0.45-0.60 mmol organic/g of deriva-tized silica were obtained for a series of para-substituted α,ω-diphenylalkanes (Fig. 1). These coverages correspond to ca. 1.5 - 2.0 organic molecules/nm^2 surface area, or 35-45% derivatization of the ca. 4.5 surface OH/nm^2 available. An examina-tion of these surface coverages with the use of model crystalline silica surfaces suggested a "liquid-like" monolayer with steric constraints prohibiting signifi-cantly higher coverages.[4]

Thermolysis Methodology.[4,5] Thermolyses were performed in sealed, evacuated (2 × 10^{-6} torr) T-shaped pyrex tubes in a configuration such that volatile products could be collected in a cold trap (77 K) as they formed. These products were analyzed by GC and GC-MS with the use of internal standards. In a separate procedure, surface-attached products were liberated as phenols following digestion of the silica in base, silylated to the corresponding trimethylsilyl ethers, and analyzed as above.

Thermolysis of Diarylalkanes. The surface-attached diphenylalkanes, ≡SiOC$_6$H$_4$(CH$_2$)$_n$C$_6$H$_5$ [n = 0-4] (represented as ~~Ph(CH$_2$)$_n$Ph) were prepared, and their thermolysis behavior compared with that of the parent hydrocarbons in fluid phases. Major findings will now be briefly surveyed.

(1) Biphenyl and diphenylmethane are thermally stable at 400°C for many hours.[2] Heating ~~PhPh and ~~PhCH$_2$Ph at 400°C for 4 h showed only the evolution of 5-10% of the parent phenols into the cold trap. This minor reaction is analogous to the well-known dehydroxylation of silica itself, and the results indicated that this mode of surface attachment is robust enough to keep most of the organic moieties on the surface for several hours at 400°C. Most importantly, no new products, either volatile or surface-attached, were observed and, hence, the silica surface (e.g., residual surface hydroxyls) did not induce any new reaction pathways. This factor allows for the study of the influence of restricted diffusion on thermolysis reactions in the absence of other possible surface-induced perturbations.

(2) Studies of surface-immobilized bibenzyl[4] (~~PhCH$_2$CH$_2$Ph, or ~~BB) revealed that the unimolecular homolysis rate for the central C-C bond was independent of surface coverage and not affected by the mode of surface attachment. Analysis of the rate constants at 350-400°C gave activation parameters, E_a = 62.9 ± 1.8 kcal/mol and A = 10$^{(15.3\pm0.6)}$s^{-1}, that are comparable to fluid phase values. A comparison of the homolysis rate constants for gaseous,[8,9] liquid (tetralin),[8,10] and surface attached bibenzyl at 375°C are thus 2.2 × 10^{-6}, 1.1 × 10^{-6}, and 1.2 × 10^{-6} s^{-1}, respectively. Although more examples are needed, these results give added confidence to the extrapolation of bond homolysis rates for ArCH$_2$CH$_2$Ar' model compounds to comparable dimethylene bridges in coal.

Studies of ~~BB also showed that dramatically altered product distributions can result from diffusional constraints. This is illustrated in Fig. 2, which compares the major product selectivities for ~~BB at high surface coverage (0.465 mmol/g) with that of liquid BB at comparable low conversions (ca. 1.5%). The major finding was that restricted diffusion enhances the rates of free-radical chain processes on the surface that result in rearrangement [to ~~PhCH(Ph)CH$_3$] and cyclization [to ~~dihydrophenanthrene and ~~phenanthrene] of ~~BB. The kinetic chain length for rearrangement was enhanced some 30-fold compared to liquid-phase BB. Note also that some of the hydrogen eliminated (or transferred) during the cyclization-dehydrogena-tion process induced significant amounts of cleavage of the much stronger C$_{ar}$-C$_{al}$ bonds. The enhanced rates of chain rearrangement and cyclization (which cycle through ~~PhCH•CH$_2$Ph and ~~PhCH$_2$CH•Ph) were closely coupled to a dramatically

decreased rate for radical-radical coupling on the surface, which would likely serve as an important chain termination step. This is evidenced by the disappearance of tetraphenylbutanes as thermolysis products on the surface, whereas they were major products in the liquid BB reaction (Fig. 2). The rearrangement and cyclization reactions provide retrogressive pathways toward more refractory materials during coal pyrolysis. In coal liquefaction, good hydrogen donor solvents (DH) may play an additional role of chain inhibitor by transferring radical centers from immobilized ArCH·CH$_2$Ar' to D·, which are free to diffuse and terminate chains.

(3) Earlier studies of fluid phase 1,3-diphenylpropane (DPP)[11,12] were important in establishing that C$_3$-links between aromatic and heteroaromatic clusters in coal could decay at significant rates at 350-400°C as a result of a free-radical chain decomposition pathway, even though the weakest C-C bond in DPP has a bond strength of ca. 74 kcal/mol. Our recent studies of surface-attached DPP suggested that these types of linkages can also decay efficiently in this temperature regime even under conditions of restricted diffusion.[5] ~~DPP thermally cracked to give two sets of products (the two ends of the molecule are dissimilar) as shown below.

~~Ph(CH$_2$)$_3$Ph → ~~PhCH$_3$ + PhCH=CH$_2$ and   ~~PhCH=CH$_2$ + PhCH$_3$
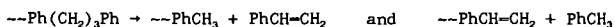
The chain propagation steps are shown in Fig. 3 where the parentheses in the hydrogen transfer step indicate that both vapor-phase and surface-attached species undergo the reaction. The overall rate of decomposition of ~~DPP at high coverages (7-9 %/h at 375°C, 0.57-0.59 mmol/g) is comparable to that of liquid DPP. However, the rate was found to be even more sensitive to surface coverage than the rate of fluid-phase DPP thermolysis is to concentration with the rate decreasing to 0.26 %/h at the lowest coverage studied (0.102 mmol/g). The restricted mobility also induced regioselectivity in the thermolysis of ~~DPP. The regioselectivity is determined by the relative concentration of the two benzylic radicals, [~~PhCH$_2$CH$_2$CH·Ph]/ [~~PhCH·CH$_2$CH$_2$Ph], and can be experimentally monitored by the PhCH=CH$_2$/PhCH$_3$ yield ratio, S. In related fluid phase studies of Me$_3$SiOPh(CH$_2$)$_3$Ph[13], a slight inherent substituent effect, S = 0.91, was observed, indicating a slight stabilization of the benzylic radical para to the siloxy substituent. The corresponding inherent selectivity for ~~DPP at high surface coverages from data extrapolated to zero ~~DPP conversion was ca. 0.95. However, the selectivity gradually increased (S > 1.0) with increasing conversion and decreasing initial surface coverage. For example, at a coverage of 0.10 mmol/g and a ~~DPP conversion of 2.8%, we found S = 1.30. It appears that as ~~DPP molecules become increasingly distant from hydrogen abstracting radicals on the surface, geometrical constraints induced by the restricted mobility begin to favor hydrogen abstraction at the benzylic methylene site farthest from the surface as illustrated in Fig. 4. Hence, the efficiency and regioselectivity in the thermal cleavage of such linkages in coal will likely depend on their immediate environment and on the presence or absence of mobile radical sources.
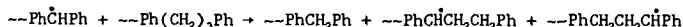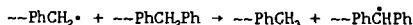
(4) Studies of surface-attached 1,4-diphenylbutane (~~DPB) are now being pursued to further explore the regioselectivity of hydrogen transfer induced by restricted mobility.[8] As shown in Fig. 5, ~~DPB decays readily at 400°C to four sets of products via a radical chain process analogous to ~~DPP, which cycles through radicals at the four distinct positions labeled in the polymethylene chain. The selectivity for the products derived from the two benzylic carbon radical sites, 4/1 (as measured by PhCH=CH$_2$/PhCH$_2$CH$_3$ yield ratio) increases with increasing conversion and decreasing surface coverage as did the analogous selectivity for ~~DPP. However, ~~DPB also shows substantial cracking occurring through nonbenzylic radical counterparts. Clearly at high surface coverage all four cracking pathways are competitive (Fig. 5). Our accumulating evidence indicates that rapid hydrogen transfer reactions with parent ~~DPB allow interconversion of benzylic and non-benzylic radical sites. [The nonbenzylic radicals actually have faster rates for β-

scission, and an analogous proposal for radical interconversion has been made for the case of fluid phase DPB.[11]]

e.g.,   ~~1-DPB· + ~~DPB ⇌ ~~DPB + ~~2-DPB·
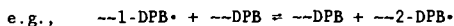
This concept of rapid hydrogen transfer reactions occurring on the surface is supported by studies of ~~DPB at lower surface coverages, which hinder the radical interconversion process. For example, decreasing the surface coverage from 0.541 to 0.054 mmol/g substantially increases the 1/2 selectivity (measured from PhCH$_2$CH$_3$/ PhCH$_3$ ratio) from 1.18 to 2.01. Additional supporting evidence is obtained from current studies of two-component surfaces described below.

(5) Two-component surfaces containing ~~DPP with co-attached aromatics (shown in Fig. 6) were prepared having coverages for ~~DPP and the co-attached aromatic in the ranges of 0.10-0.17 mmol/g and 0.37-0.51 mmol/g, respectively. The results showed that the rate and regioselectivity of ~~DPP thermolysis is dependent on the structure of neighboring molecules on the surface. While the presence of ~~BP or ~~NAP has only small effects·on the ~~DPP thermolysis compared with ~~DPP alone at similar surface coverages, the presence of ~~DPM dramatically alters both the rate and regioselectivity of the ~~DPP reaction. For single component samples of ~~DPP with coverages of 0.566 and 0.142 mmol/g, the ~~DPP conversion rates at 375°C were 6.6 and 0.39 %/h respectively. On the other hand a material containing ~~DPP/~~DPM (0.133/0.368 mmol/g) gives a ~~DPP thermolysis rate of 5.8 %/h, the same as high coverages of ~~DPP within our experimental error. Moreover, values for the regioselectivity, S, for this two component surface are in the range of 0.95 (similar to high coverages of ~~DPP at low conversions) with little dependence on ~~DPP conversion. These results along with supporting evidence from related studies using the deuterated analog, ~~DPM-d$_2$, strongly suggest that facile hydrogen transfer reactions involving ~~DPM are allowing radical centers to "migrate" on the surface, e.g.:

~~PhCH$_2$· + ~~PhCH$_2$Ph → ~~PhCH$_3$ + ~~PhĊHPh

~~PhĊHPh + ~~Ph(CH$_2$)$_3$Ph → ~~PhCH$_2$Ph + ~~PhCĤCH$_2$CH$_2$Ph + ~~PhCH$_2$CH$_2$ĊHPh

The result of such a process is to effectively decrease the distance between a ~~DPP molecule and a radical center on the surface. Not only does this enhance the rate at which ~~DPP reacts (compared with ~~DPP alone at a similar low surface coverage), but it also eliminates the distance-dependent conformational constraints on the hydrogen abstraction reactions from ~~DPP that lead to the regioselectivity in product formation. We have now observed similar effects in studies of ~~DPB/~~DPM (0.060/0.465 mmol/g), in which the 1/2 selectivity (1.17) is again substantially quenched and more characteristic of high surface coverages of ~~DPB (see above). The observation of facile hydrogen shuttling on the surface has important implications for coal pyrolysis. It provides evidence for a chemical means for "mobilizing" radical centers in a diffusionally constrained environment, which could have a substantial impact on the efficiency with which similar structural features would be cleaved in coal.

SUMMARY

The technique of model compound immobilization by covalent surface attachment is providing valuable insights into the role of restricted diffusion on thermal reaction pathways, which could be of relevance to coal and other macromolecular

systems. This methodology should be readily extended to the study of other chemical systems of interest, and to probing other mechanistic aspects of the thermal chemistry of coal.
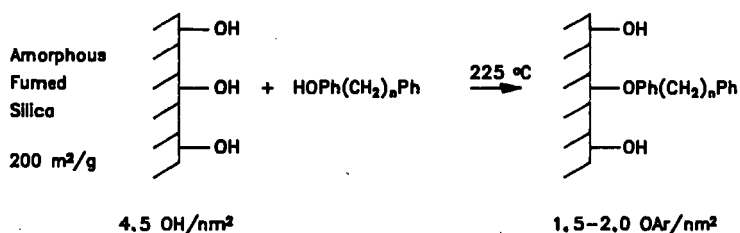
ACKNOWLEDGEMENTS

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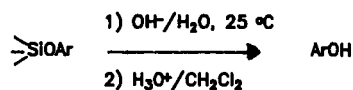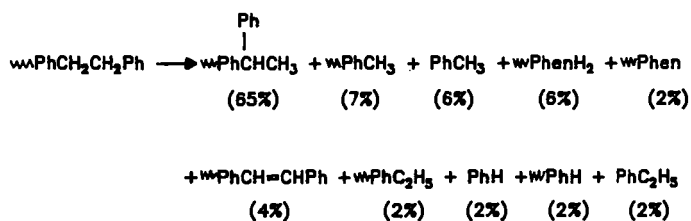
Figure 1. Surface Attachment Reaction

Amorphous Fumed Silica

200 m²/g

⌐OH

⌐OH + HOPh(CH₂)ₙPh $\xrightarrow{\text{225 °C}}$

⌐OH

4.5 OH/nm²

⌐OH

⌐OPh(CH₂)ₙPh

⌐OH

1.5–2.0 OAr/nm²

Surface Coverage Analysis:

$\geq$SiOAr $\xrightarrow[\text{2) } H_3O^+/CH_2Cl_2]{\text{1) } OH^-/H_2O,\ 25\ °C}$ ArOH

Figure 2. Effect of surface–immobilization on bibenzyl thermolysis

[Surface–immobilized]

wwPhCH₂CH₂Ph $\longrightarrow$ wwPhCHCH₃ (with Ph above) + wwPhCH₃ + PhCH₃ + wPhenH₂ + wPhen

(65%)   (7%)   (6%)   (6%)   (2%)

+ wwPhCH=CHPh + wwPhC₂H₅ + PhH + wPhH + PhC₂H₅

(4%)   (2%)   (2%)   (2%)   (2%)

[Liquid]

PhCH₂CH₂Ph $\longrightarrow$ PhCH₃ + (PhCH₂CHPh→)₂ + Ph₂CHCH₃ + PhCH=CHPh

(56%)   (23%)   (10%)   (9%)
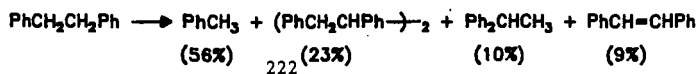
Figure 3. Radical chain propagation steps for ∿DPP

∿ Ph(CH$_2$)$_3$Ph + (∿)PhCH$_2$ •

⟶ ∿ PhĊHCH$_2$CH$_2$Ph + (∿)PhCH$_3$

⟶ ∿ PhCH$_2$CH$_2$ĊHPh + (∿)PhCH$_3$

∿ PhĊHCH$_2$CH$_2$Ph ⟶ ∿ PhCH=CH$_2$ + PhCH$_2$ •

∿ PhCH$_2$CH$_2$ĊHPh ⟶ ∿ PhCH$_2$• + PhCH=CH$_2$
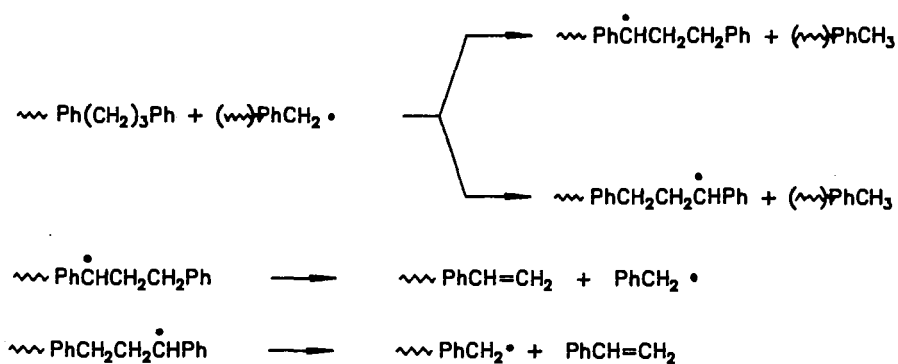
Figure 4. Regiospecific Hydrogen Transfer
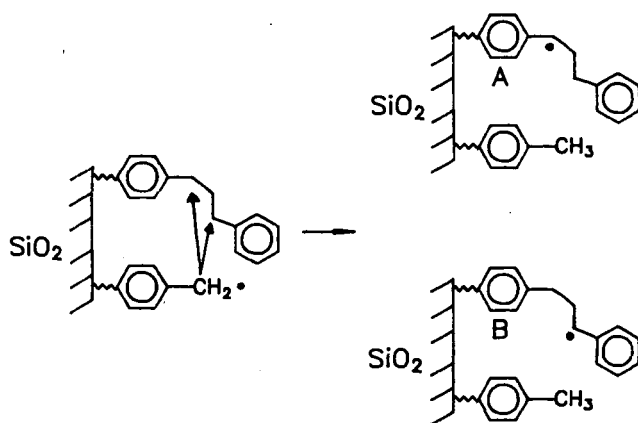
Figure 5. Thermolysis of ∿Ph(CH$_2$)$_4$Ph at 400 °C ;

Selectivity: (1) 1.18 (2) 1.00 (3) 1.09 (4) 1.22

1 2 3 4
∿∿ PhCH$_2$CH$_2$CH$_2$CH$_2$Ph

(0.54 mmol/g)

(2.4% conv in 10 min)

1 → ∿∿ PhCH=CH$_2$ + PhCH$_2$CH$_3$

2 → ∿∿ PhCH$_2$CH=CH$_2$ + PhCH$_3$
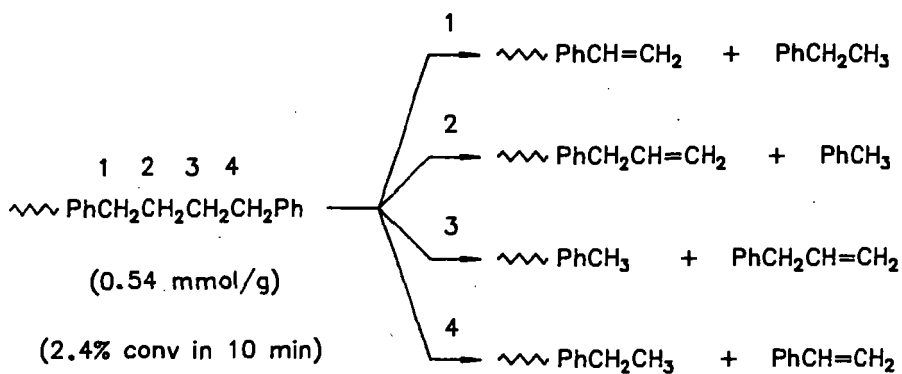
3 → ∿∿ PhCH$_3$ + PhCH$_2$CH=CH$_2$

4 → ∿∿ PhCH$_2$CH$_3$ + PhCH=CH$_2$

Figure 6. Two-component surfaces studied

∿∿DPP / ∿∿BP   ∿∿DPP / ∿∿NAP   ∿∿DPP / ∿∿DPM